Gas Cleanup and Conditioning: Catalyst Fundamentals

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- Project Background
  - Stage Placement
  - Objectives
  - Milestones
  - Budget
- Technical Feasibility and Risks
- Competitive Advantage
- History and Accomplishments
- Plan/Schedule
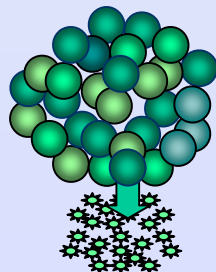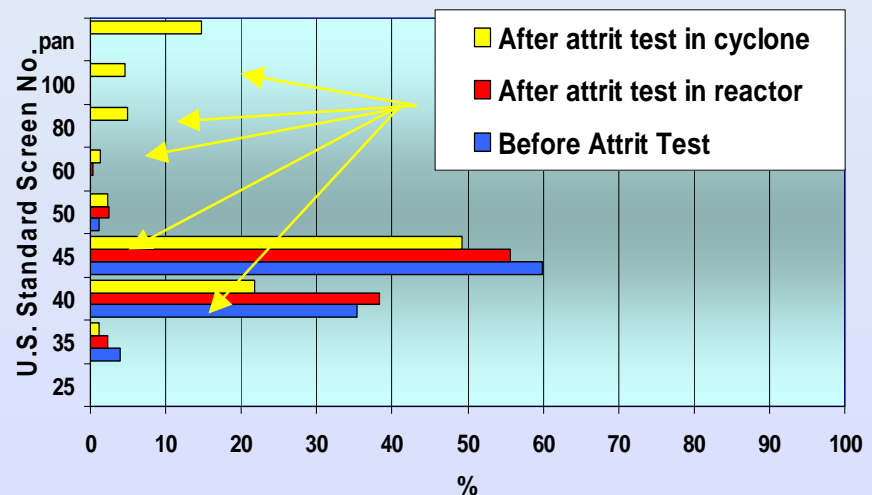- Critical Issues and Show-stoppers
- Summary

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- Tars and methane in biomass-derived syngas must be removed via reforming reactions to produce conditioned syngas

- Reforming complex syngas compositions requires fluidization

- Commercial reforming fluidizable catalyst are not available and fluidizable reforming catalysts need to be developed

Particle Size Distribution Al-5

Particles from fixed bed commercial catalysts attrit when fluidized

Legend:
- After attrit test in cyclone
- After attrit test in reactor
- Before Attrit Test

Y-axis: U.S. Standard Screen No. (pan, 100, 80, 60, 50, 45, 40, 35, 25)

X-axis: % (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100)

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Stage "A/B"

- Supports other projects and provides information on catalyst performance for use in micro-, lab-, and pilot-scale systems and techno-economic assessments

Develop long duration catalyst activity to maintain syngas quality (tar destruction >99%) to meet accepted gas quality standards.

Technical Challenges

- Improve cracking/reforming catalyst performance
    - Develop attrition resistant reforming catalysts
    - Scale catalyst production
    - Reduce/change metallic components
    - Characterize and understand catalyst behavior
    - Predict pilot scale behavior from MATS behavior
    - Multivariate catalyst design

- Optimize catalyst regeneration
    - Understand/minimize catalyst deactivation

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Ag Residues　　**Perennial Grasses**　　　　**Pulp and Paper**　　**Forest Products**
　　　　　　　　　　Woody Crops

Validate Cost-effective Gas Cleanup Performance
Supports 6 "C" Milestones

| M4.11.3 | M5.11.3 | M5.12.3 |
| M4.11.5 | M5.11.5 | M5.12.5 |

Project Milestones	Type	Performance Expectations	Due Date
Tar reforming catalyst screening and optimization	D	Identify candidate materials for additional testing by screening 25 catalyst formulations for optimal catalyst characteristics in micro scale test system 1, testing 10 of the best candidates for reforming activity in micro scale test system 2, and correlate results with available fluidized bed and full stream reforming catalyst studies to identify superior reforming catalysts for future full stream reactor testing.	June 2005

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Technical Feasibility

- Support suppliers exist; several groups developing catalysts

- Analytical technology for rapid catalyst preparation, analysis and screening operational

Technical Risks

- Catalyst reforming performance requires improvement (complex syngas compositions)

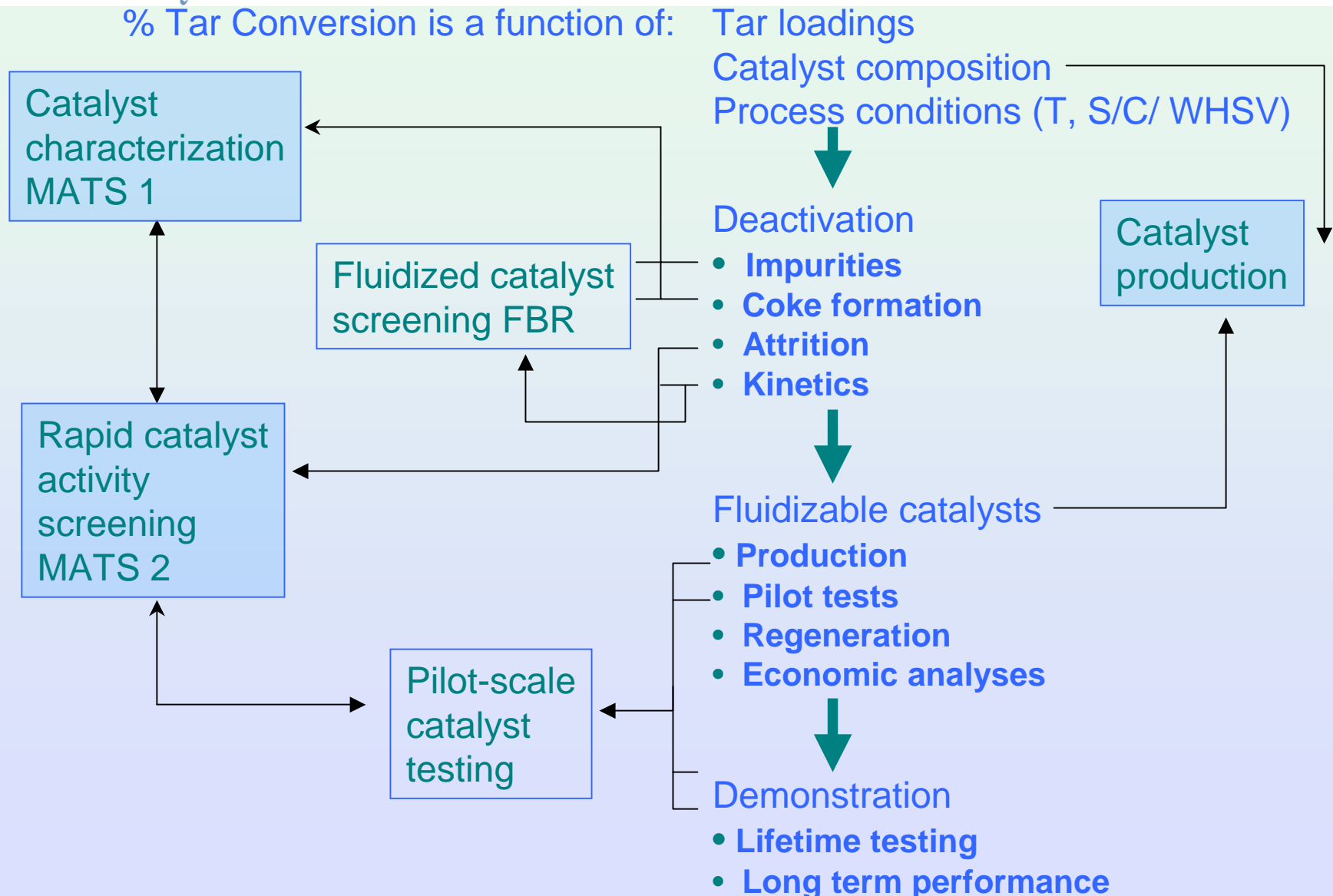- Impurities impact catalyst performance; S removal technologies exist

- How will this project improve the chances of commercial launch of the technology?

- No commercial fluidizable reforming catalysts available; developing efficient gas conditioning catalysts for commercial syngas cleanup requirements

- Rapid catalyst synthesis and screening to optimize catalysts

- High throughput catalyst screening transferable to pilot-scale studies

- Understand syngas composition impact on catalyst performance

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% Tar Conversion is a function of: Tar loadings
Catalyst composition
Process conditions (T, S/C/ WHSV)

Catalyst characterization MATS 1

Fluidized catalyst screening FBR

Deactivation
- **Impurities**
- **Coke formation**
- **Attrition**
- **Kinetics**

Catalyst production

Rapid catalyst activity screening MATS 2

Fluidizable catalysts
- **Production**
- **Pilot tests**
- **Regeneration**
- **Economic analyses**

Pilot-scale catalyst testing

Demonstration
- **Lifetime testing**
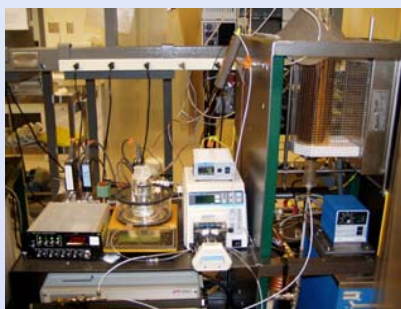- **Long term performance**

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Gas Conditioning Catalyst Development

MATS 1
➢ Fixed bed 1 g catalyst
➢ Catalyst characterization
➢ Temperature programmed reaction, oxidation, reduction

Rapid catalyst preparation

MATS 2
➢ Fixed bed 1 g catalyst
➢ Tar destruction
➢ Steam reforming
➢ TCPDU slipstream

2" FBR
➢ Fluid bed 250 g catalyst
➢ Kinetic data
➢ Lifetime data
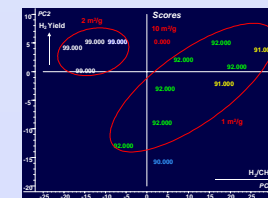➢ TCPDU slipstream
➢ Comprehensive online analysis

TCPDU
➢ Fluid bed 50 kg catalyst
➢ Process data
➢ Kinetic data
➢ Lifetime data
➢ Online analysis

Multivariate Models
➢ Guide catalyst optimization

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Project Tasks

- Produce catalyst material (lab – pilot scale)
    (0.1-100 kg)

- Catalyst screening via Micro Activity Test Systems (MATS) to rapidly:
    - characterize catalysts (TPR)
    - screen catalyst reforming activity
    - determine reforming kinetics
    - develop regeneration profiles
    - determine impurity impacts

- Determine catalyst reforming kinetics at slipstream and full stream studies

- Develop multivariate catalyst design via data linkage and mining

Catalyst Preparation

- Performance requirements

Tar reforming:	$CxHyOz + H_2O(g) \rightarrow H_2 + xCO$
Water gas shift:	$H_2O + CO \longrightarrow CO_2 + H_2$
Coke gasification:	$C + H_2O(g) \longrightarrow COx + H_2$
Steam methane reforming:	$CH_4 + H_2O \longrightarrow CO + 3H_2$

- NREL Batch size: 0.1-100 kg (larger scale with industrial collaborators)
- Support type/treatment/particle size/surface area
- Catalyst components and promoters
- Preparation

  Incipient wetness
  Calcination
  Reduction

75-kg Catalyst Preparation

Catalyst solution

CoorsTek Support

Hazen Auger Calciner

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Ni crystals
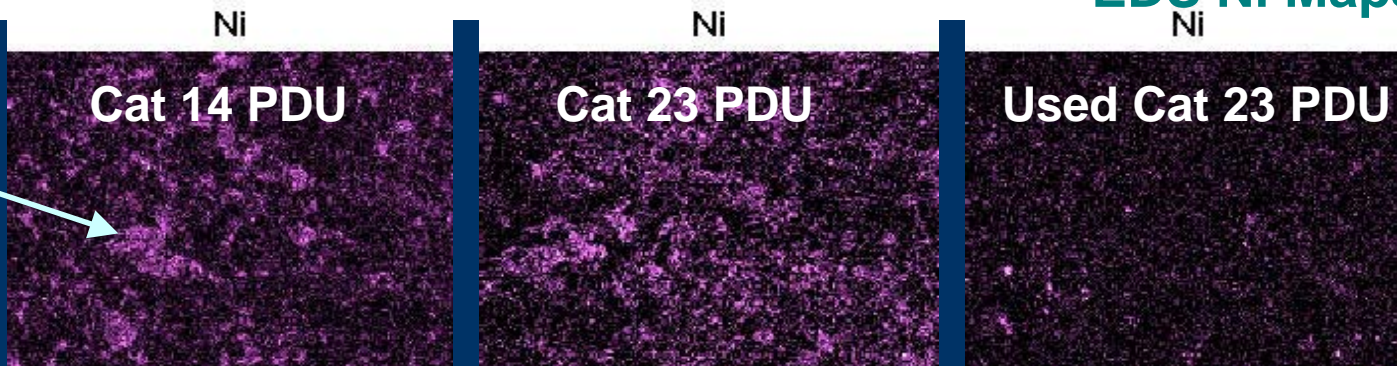
Catalyst	Catalyst SA m^2/g	NiO wt%	MgO wt%	K_2O wt%
Cat 14	0.9	2	0.2	0.4
Cat 23	1.0	2	0.2	0.4
Cat 23 used	0.8	2	0.2	0.4
C 11 NK	11.0	20.0	15.0	7.0
Cat 26	0.6	6	1.0	4.0
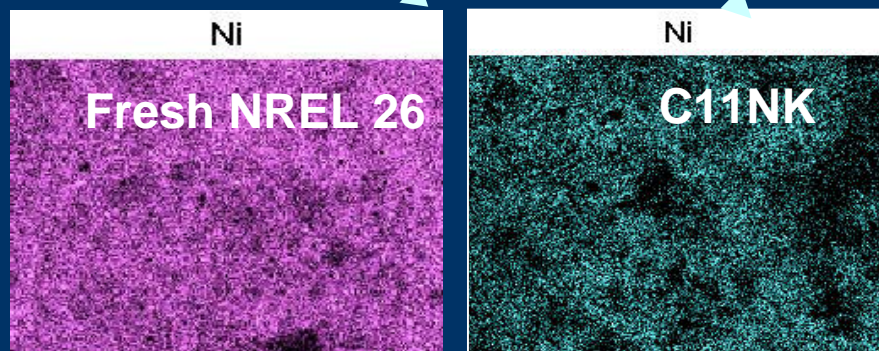
Similar Ni dispersions
- NREL cats have less Ni
- Economic, process, and environmental impacts
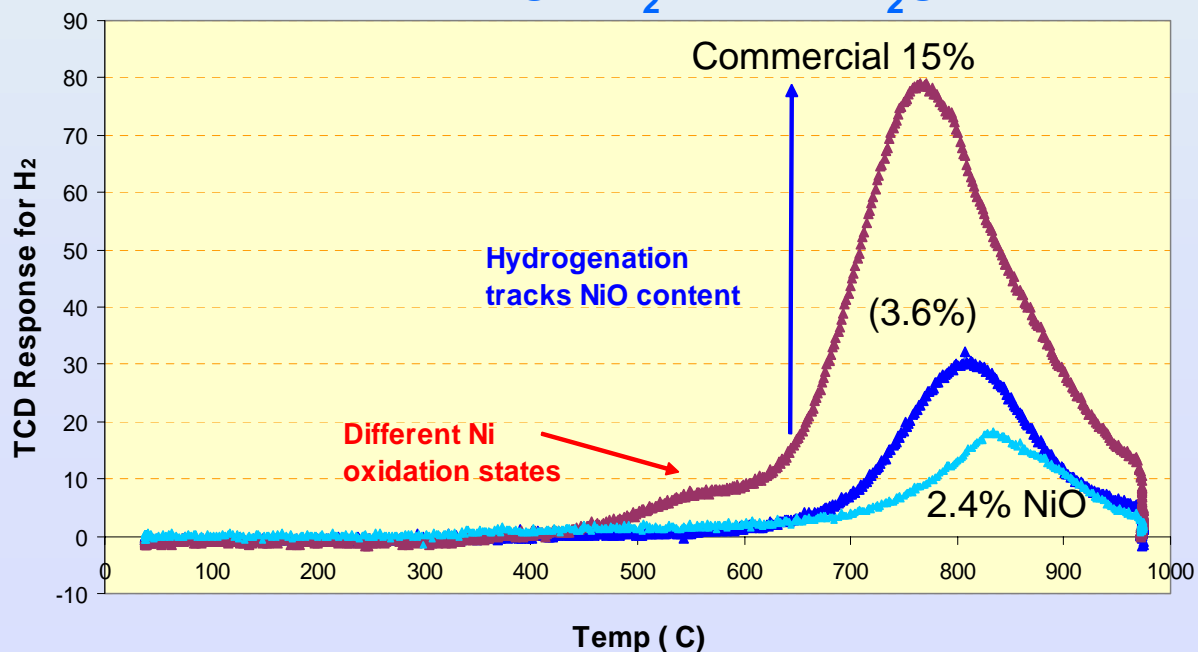
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MATS 1

MATS 1 provides:

- Catalyst fingerprint
- TPR probes
- Regeneration profiles
- Impurity impacts
- Deactivated catalyst analysis

MATS 1 Characterization

MATS 1 shows:
- Ni reduction scales with content
- NREL catalysts similar to commercial catalysts
- Need to optimize preparation: varied Ni states- MATS 2 for kinetics
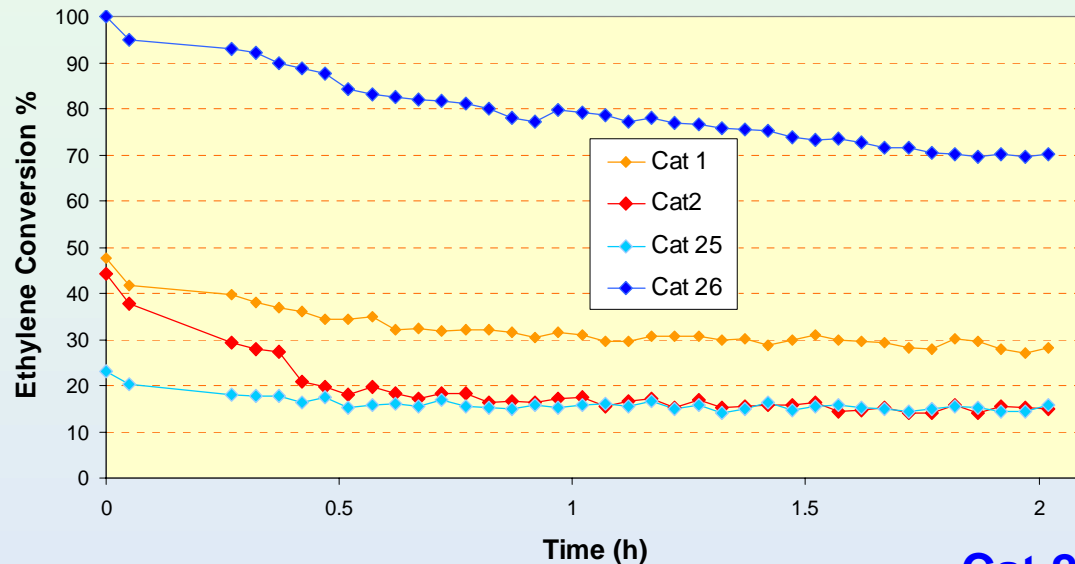
$$NiO + H_2 \longrightarrow Ni + H_2O$$

Commercial 15%

Hydrogenation tracks NiO content

(3.6%)

Different Ni oxidation states

2.4% NiO

TCD Response for H_2

Temp (C)

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MATS 2 Screening: Reforming Activity

- Defining reaction space
- Rank catalyst performance
- Reforming kinetics
- Correlate with MATS 1 and FBR data

Cat 26 chosen for PDU Tests

Catalyst	Alumina %	NiO wt%	MgO wt%	K_2O wt%
Commercial	Mix	20.0	15.0	7.0
Support 90% Al_2O_3	90	0.0	<3.0	<1.0
NREL Cats 1-26	90, 99	<10.0	<5.0	<5.0

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Project plans and schedule

- Complete Milestone - June 2005

- Develop multivariate models for catalyst composition (FY05-06)

- Evaluate physical properties of commercial fluidizable supports (FY06)

- Evaluate S (impurities) and deactivation impacts on catalyst performance (FY06)

- Identify optimum catalyst composition for gas conditioning target and syngas composition (FY07)

- Identify industrial catalyst suppliers (FY07)

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- ## Critical performance parameters
  - Meet gas conditioning goals with varied catalyst compositions and syngas compositions
  - Support availability
  - Design impurity tolerance

- ## Potential show-stoppers
  - Cost effective gas conditioning goals
  - Impurities (S, Cl)

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If this project is successful; what's next, commercialization partners?

- Identify and test other supports
- Develop catalysts for complex syngas compositions
- Catalyst manufacturers (provide catalysts)
- Gasification developers (users)

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- Evaluate/optimize new support compositions and catalysts with varied syngas compositions

- Novel screening tools coupled with multivariate analysis to guide catalyst composition

- Develop catalyst/performance database
  - NREL, commercial, developing catalysts

- Characterize/re-evaluate used pilot scale catalysts; understand deactivation

- Develop impurity tolerance

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Year	Funding History - $K
FY2005	953
FY2006	1000

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Stefan Czernik
Rick French
Yves Parent
Matt Ratcliff

CoorsTek
  Steve Landin

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